

Solutions to Exercises – chapter 7

7.1) Explain the basic differences between atomic emission and atomic absorption spectroscopy.

Atomic spectroscopic techniques are broadly classified as either being based upon atomic emission or atomic absorption processes. Atomic emission spectroscopy involves the emission of photons as electrons relax from excited states back to their ground states. Atomic absorption techniques by contrast, are based upon the capture of photons, as electrons are promoted or even lost in the formation of an ion.

7.2) Why are hollow cathode lamps used in preference to other radiation sources?

Atomic absorption bandwidths are extremely narrow, typically being in the order of $<0.01\text{nm}$. It is especially important that the light source used is capable of producing radiation centred at exactly the correct wavelength and with an extremely narrow bandwidth. This can be achieved by use of a hollow cathode lamp, which is a gas discharge lamp that exploits the emission characteristics of the same element to be monitored.

7.3) Explain what is meant by (i) Doppler and (ii) Pressure broadening.

- (i) The Doppler effect observed when an apparent wavelength change occurs on moving quickly towards or away from a sound source is well known. Doppler shifts are observed in atomic spectroscopy leading to apparent shifts in the wavelengths at which atomic absorption or emission lines are observed. This leads to their broadening. This phenomenon occurs due to the emitting or absorbing species travelling at high velocities as a result of thermal excitation from the flame or plasma.
- (ii) Collisions between the emitting or absorbing species with other atoms or ions lead to small changes in ground-state energy levels, and hence a spread in the wavelengths of the absorbed or emitted radiation. These effects are sometimes known as pressure broadening. Within a flame, the collisions occur largely between the atoms of the analyte and various combustion products of the fuel - and these may result in broadening of two or three orders of magnitude over the natural line widths. Similar effects are often observed as a consequence of collisions within the plasma excitation media of inductively coupled plasma spectroscopy. Line broadening within hollow-cathode and electrode-discharge lamps is largely caused by collisions between the emitting atoms themselves.

7.4) Why are high temperature nitrous oxide-acetylene flames sometimes required within atomic absorption spectroscopy?

The flame is merely used to atomise the sample and for this reason the control of its temperature is crucial. Ideally we would wish to atomise the entire sample without the creation of ions which absorb light at different wavelengths. The use of air limits the maximum temperature, and if temperatures greater than around 2200°C are required nitrous oxide can be used instead of air to allow temperatures of up to approximately 3000°C to be achieved.

7.5) What are the relative advantages and disadvantages of using ICP torches?

ICP approaches can offer greater sensitivity than can be otherwise obtained and this can offer advantages if the determination of trace elements is required. Chemical interferences tend to be less significant however with arc atomic spectroscopy however due to the high temperature within the arc.

7.6) A 10ppm solution of lithium gives an atomic absorption signal of 12% absorption; what is the atomic absorption sensitivity?

$$A = \epsilon cl \therefore A \propto c$$

10ppm corresponds to 12% absorption. \therefore 1ppm would correspond to $\frac{12}{10}\%$ =

1.2%

It follows that the atomic absorption sensitivity corresponds to an increase of 1.2% absorption for every 1ppm increase in lithium concentration.

7.7) Explain why atomic emission spectra consist of discrete lines rather than broad bands.

The promotion and relaxation of valence electrons can give rise to UV/visible and fluorescent spectroscopy. It is the valence electrons which are involved with the bonding whether it be ionic or covalent in nature. The bonding orbitals and therefore the electrons are primarily associated with the compound and not an individual atom *per se*.

Atomic spectroscopic approaches involve and exploit the electronic transitions of electrons not involved in bonding – ie: either non-valence electrons within atoms or compounds (or the valence electrons of elemental atoms or ions). Atomic spectra originate from electronic transitions between *atomic* or *elemental* ionic orbitals and give rise to extremely narrow absorption lines, with wavelength band widths typically in the order of 0.1nm or so.

7.8) A drinking water supply is suspected of being contaminated with lead. Samples of water aspirated directly into an air/acetylene flame gave an absorbance of 0.68 at 283.3nm. Standard solutions containing 0.5 and 1.0 ppm were found to exhibit absorbances of 0.43 and 0.86 respectively. Assuming the Beer-Lambert law is obeyed calculate the concentration of lead within the water sample.

Absorbance of 0.68 at 283nm for drinking water sample.

Standard solution of 0.5 gives an absorbance of 0.43

Standard solution of 1.0ppm gives an absorbance of 0.86

An increase of 0.5ppm gives rise to an increase in absorbance of 0.86-0.43

$$\therefore A = 0.43$$

An addition of 0.5ppm gives an absorption of 0.5

It follows the baseline must be equal to $0.43 - 0.43 = 0.0$

It also follows that the sample of drinking water corresponds to a concentration of:

$$\frac{0.68}{0.43} \times 0.5 \text{ppm} = 0.79 \text{ppm Pb}$$

7.9) Explain why sharp line radiation sources are desirable for atomic absorption spectroscopy.

Sharp line radiation sources should be used to ensure selectivity for a particular element. Ideally the emission wavelength bandwidth for the radiation source should be narrower than the absorption bandwidth for the analyte.

7.10) Describe the principles underlying flame emission atomic spectroscopy.

- Flame atomic absorption spectroscopy is widely used to determine trace levels of metals within different types of sample.

- A supply of atoms in the elemental (or free elemental ionic form) must be provided.
- This is achieved via a nebuliser (Fig 7.1 in book) in conjunction with an air/acetylene flame. This produces a micro-droplet aerosol of the analyte solution.
- The combustion gases are mixed prior to combustion (Fig 7.2 in book). The flame is directed through a gas jet and burns at a temperature of approximately 2000-2200°C. Higher temperatures may be achieved via the use of a nitrous oxide / acetylene fuel gas mixture.
- The solvent evaporates very quickly and metal ion salts will be easily reduced. This completes the atomisation process. A detector (eg a photomultiplier tube) then monitors the intensity of the radiation and so any absorption that occurs.
- A highly monochromatic incident radiation source (viz a hollow cathode lamp) is directed towards the flame. The detector is arranged so as to monitor the intensity of the radiation transmitted through the flame (figure 7.3 of book). A reference beam and chopper system is often employed to prevent distortion of the monitored signal from ambient radiation.

7.11) Explain how and why reference standard materials are often used within both atomic absorption and emission spectroscopic techniques.

The absorption of different flame spectrophotometers may vary considerably from one instrument to another with the same type of sample. This behaviour differs considerably from UV-visible spectroscopy where we would expect the readings from one instrument to concur with another.

We can calibrate individual instruments however using suitable reference materials and so obtain reliable measurements since the behaviour of an individual instrument should be reproducible. Certified reference materials may also be added to the sample in the form of a standard additions calibration.

7.12) A serum sample is analysed by flame emission spectroscopy for potassium using a standard additions approach. Two 1ml additions are added to 10ml aliquots. 20 μ l of a 0.025M KCl solution is added to water sample A. The emission signals in arbitrary units of the two water samples A and B are determined to be 88.5 and 58.9 respectively. Calculate the concentration of K⁺ within the serum.

The total volume for each sample is 11ml.

We can assume that the 20 μ l addition does not alter the volume of the sample it is added to.

20 μ l of 0.025M KCl is equivalent to: $20 \times 10^{-6} \times 0.025$ moles KCl.

$$= 5 \times 10^{-7} \text{ moles KCl or K}^+$$

5×10^{-7} moles of KCl are contained in 11ml sample.

This corresponds to an increase of:

$$\frac{5 \times 10^{-7}}{11} \times 1000 \text{ moles dm}^{-3} = 4.54 \times 10^{-5} \text{M}$$

An increase in $[\text{K}^+]$ is equivalent to an increase in signal of 88.5-58.9 arbitrary units = 29.6 units.

The concentration of K^+ within the 11ml is therefore:

$$\frac{29.6}{32.6} \times 4.54 \times 10^{-5} \text{ mol dm}^{-3} = 4.122 \times 10^{-5} \text{ M}$$

The original volume was however 1 ml so:

$$\text{the original } [\text{K}^+] = 4.122 \times 10^{-5} \times 11 \text{ mol dm}^{-3}$$

$$\underline{[\text{K}^+] = 4.53 \times 10^{-4} \text{M}}$$

7.13) The sodium (Na^+) content of a brine solution is to be analysed by flame emission spectroscopy. Two 5 cm^3 additions are added to 10 cm^3 distilled water. The first of these samples exhibits an emission of 3310 (arbitrary units). The second sample has 50 μ l of a 0.1M NaCl solution added prior to analysis; this exhibits an emission of 3550 arbitrary units. Calculate the concentration of NaCl within the brine solution.

The addition of 50 μ l 0.1M NaCl causes an increase in signal of 3550-3310 = 240 units.

50 μ l of 0.1M NaCl is equivalent to:

$$50 \times 10^{-6} \times 0.1 \text{ moles NaCl}$$

$$= 5 \times 10^{-6} \text{ moles NaCl}$$

We can assume that an addition of 50 μ l does not alter the volume of the sample = 15cm³

The increase in concentration will be equivalent to:

$$\frac{5 \times 10^{-6}}{15} \times 1000 \text{ mol dm}^{-3} = \text{an increase of } 3.33 \times 10^{-4} \text{ mol dm}^{-3}$$

The concentration of the sample prior to the standard addition =

$$\frac{3310}{240} \times 3.3 \times 10^{-4} \text{ mol dm}^{-3} = 4.55 \times 10^{-3} \text{ M}$$

The original sample volume was however 5ml

The original concentration was therefore $\frac{15}{3} \times 4.55 \times 10^{-3} \text{ M}$

$$[\text{Na}^+] = 2.275 \times 10^{-2} \text{ M Na}^+$$